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Phase diagram of pseudo-ternary system $KAlF_4$–K_3AlF_6–KBe_2F_5

Rong Chen*, Genhua Wu, Qiyun Zhang

Department of Chemistry, Peking University, Beijing 100871, PR China

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Abstract

For developing a new aluminum brazing flux, the liquidus in the pseudo-ternary system $KAlF_4$–K_3AlF_6–KBe_2F_5 were determined by DTA and visual poly-thermal methods. The results indicated that the ternary eutectic point E in the system melts at 310°C and located in KBe_2F_5 (81 mol%), $KAlF_4$ (15 mol%) and KF (4 mol%). The melts those contain KBe_2F_5 over 70 mol% will present glassiness during cooling. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $KAlF_4$; K_3AlF_6; KBe_2F_5; Ternary phase diagram; Nocolok brazing

1. Introduction

The pseudo-system $KAlF_4$–K_3AlF_6–KBe_2F_5 is an inner triangle in ternary system AlF_3–KF–BeF_2 as shown in Fig. 1. For two side-binary systems, AlF_3–KF [1–3], KF–BeF_2 [4,5], and two pseudo-binary systems $KAlF_4$–KBe_2F_5, K_3AlF_6–KBe_2F_5 [6] have been thoroughly investigated. The eutectic melting at 558°C in system AlF_3–KF has been widely applied as a non-corrosive, insoluble flux called Nocolok method for brazing pure aluminum and a few aluminum alloys. The drawback of this flux is that too high melting temperature for brazing most other aluminum alloys, which often have lower collapse, or over burn temperatures. So that to develop a lower melting temperature flux is a significant problem in the technology of aluminum brazing. So far as we know, some simple ionic fluorides such as alkaline-earth and rare-earth fluorides are difficulty soluble in the AlF_3–KF eutectic melt. On the other hand, the metal in fluorides with more positive electrode potential than that of aluminum will be reduced by the later during mutual reaction at higher temperature. In this situation, complex compound KBe_2F_5 expected as a hopeful candidate for adding into system AlF_3–KF to lower its eutectic temperature. The research of $KAlF_4$–K_3AlF_6–KBe_2F_5 system is just for this purpose.

2. Experimental

2.1. Preparation of fluorides and samples

The anhydrous K_2CO_3, $Al(OH)_3$, BeO and 40% HF used are all AR grades. $Al(OH)_3$ and BeO were dried at 120°C for 1 h, and K_2CO_3 dried until constant weight. Relative humidity of environment was <30%. According to the compositions of every profile, certain weight of $Al(OH)_3$ and BeO were weighed into polypropylene bickers. The samples were dissolved in excessive HF and then K_2CO_3 solution with known content was dropped in. The prepared doses were gradually heated to 100°C until dry. Then annealed for 48 h at a higher temperature such that no melting of any phase could occur. During the annealing process,

* Corresponding author. Fax: +86-10-6275-1496.
E-mail address: chenr@rose.nsfc.gov.cn (R. Chen).

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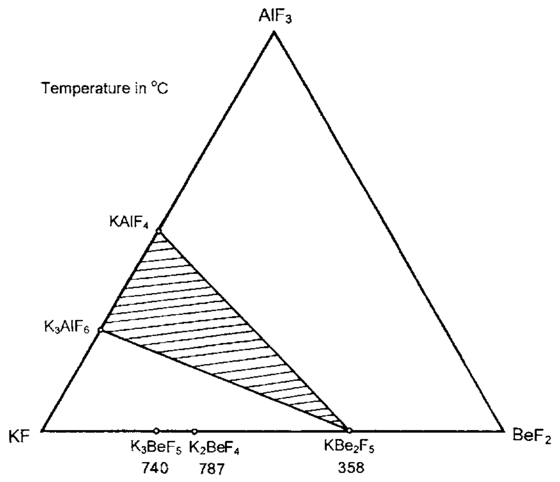

Fig. 1. Location of pseudo-system $KAlF_4$–K_3AlF_6–KBe_2F_5 in AlF_3–KF–BeF_2 system.

grinding and mixing of the samples were repeatedly carried out in order to obtain homogeneous and equilibrium samples.

2.2. Differential thermal analysis

CR-G type high-temperature DTA equipment (Beijing Optical Instrument, Inc.) was employed and calibrated by standard substances with known melting point (calibrating both, the heating and cooling curves). Baked Al_2O_3 was used as a reference substance. The heating rate was 15°C/min. Experiments were conducted in dry air (relative humidity $< 30\%$) in the static state.

2.3. Visual poly-thermal analysis

Sample was put in a 0.3 ml platinum crucible, which was welded on the tip of a Pt–PtRh thermocouple. Thermal potential was measured by a SANSE DMM 2650 digital voltmeter. Thermocouple used in the experiment was calibrated by standard substances. The melting of samples were observed under a magnifier. The error in measuring temperature was ±1°C.

3. Results and discussion

Fourteen profiles have been taken for determining the liquidus in the system $KAlF_4$–K_3AlF_6–KBe_2F_5. Terminal data of profiles listed in Table 1. Characteristic points on liquidus of profiles listed in Table 1 are shown in Table 2. Correspondent phase diagram, isotherm and side-projection are drawn in Figs. 2–4, respectively. The point ‘c’ melting at 330°C as shown in Fig. 2 is a supplementary datum, which is not produced by listed profiles.

Table 1
Terminal composition of profiles in $KAlF_4$–K_3AlF_6–KBe_2F_5 system

Profile	Terminal 1 (mol%)			Terminal 2 (mol%)		
	$KAlF_4$	KBe_2F_5	KF	$KAlF_4$	KBe_2F_5	KF
I	90	10				100
II	80	20				100
III	70	30				100
IV	60	40				100
V	50	50				100
VI	40	60				100
VII	30	70				100
VIII	20	80				100
IX	10	90				100
X	38	58	4	4	92	4
XI	94		6	6	88	6
XII	52		48	5	95	
XIII	53		47	7	93	
XIV	54		46	9	91	

Table 2
Characteristic points on liquidus of profiles in $KAlF_4$–K_3AlF_6–KBe_2F_5 system

Profile	Minimal point on liquidus			
	Composition (mol%)			Temperature (°C)
	KBe_2F_5	$KAlF_4$	KF	
I	9	81	10	510
II	18	72	10	500
III	28	63	9	490
IV	37	55	8	480
V	46	46	8	470
VI	56	38	6	460
VII	66	28	6	435
VIII	76	19	5	320
IX	85	9	6	335
X	81	15	4	310
XI	84	10	6	320
XII	84	10	6	320
XIII	83	12	5	317
XIV	82	14	4	315

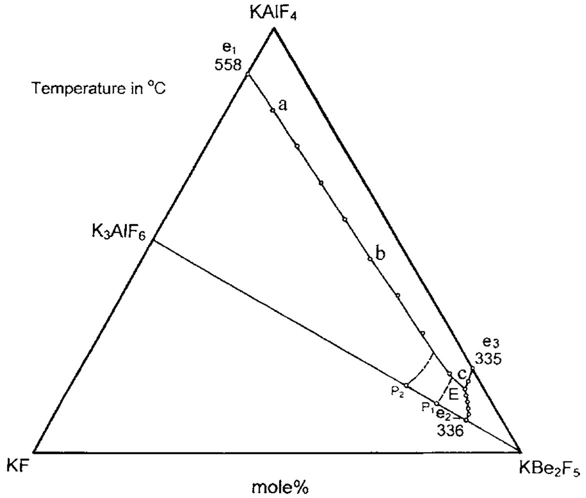

Fig. 2. Orthogonal projection of $KAlF_4$–K_3AlF_6–KBe_2F_5 system.

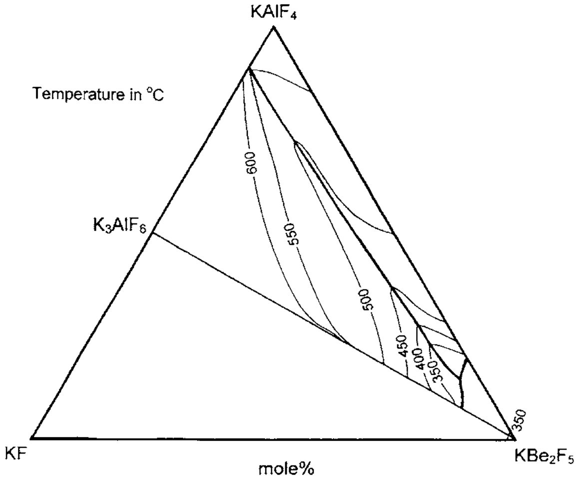

Fig. 3. Isotherm of $KAlF_4$–K_3AlF_6–KBe_2F_5 system.

From Figs. 2 and 4, it is indicated that the pseudo-ternary system belongs to a simple eutectic type. The ternary eutectic melts at 310°C, located in KBe_2F_5 (81 mol%), $KAlF_4$ (15 mol%) and KF (4 mol%). The points 'P_1' and 'P_2' are two peritectics in the binary system K_3AlF_6–KBe_2F_5 [6], but there is no ternary peritectics to be reflected in the ternary plane. So we could only draw them as two dotted lines. Along the binary eutectic line from points 'e_1' to 'E' (see Fig. 2), the melting temperature gradually decreased from 558

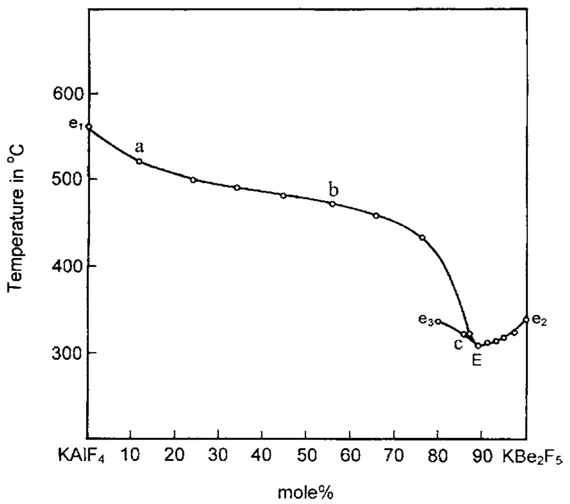

Fig. 4. Projection of pseudo-system $KAlF_4$–K_3AlF_6–KBe_2F_5 on $KAlF_4$–KBe_2F_5 side.

to 310°C (see Fig. 4) as the content of KBe_2F_5 increased. The melts those contain KBe_2F_5 over 70 mol% will present glassiness during solidifying. Meanwhile, the solubility increased. So that the hopeful composition of a flux substrate will be the interval from points 'a' and 'b' as shown in Figs. 2 and 4.

Experiments indicated that the composition between points 'a' and 'b' mentioned above is good substrates for using in aluminum brazing flux, the only problem left is its poison.

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